NOTES

Synthesis and Evaluation of Films of Methacrylates

INTRODUCTION

Free radical solution polymerization provides a route to the production of industrial polymers. Molecular weights, between 500 and 50,000, can be achieved. These polymers are used in adhesives, coatings, water treatment, pigment dispersants, detergent additives, and other applications.[1] Solution polymerization involves polymerization of monomers in the presence of a suitable solvent, which has the distinct property of dissolving the polymerized product. Therefore, the choice of solvent is important, since this choice may affect the properties of the polymer. For the copolymerization of methyl methacrylate and methacrylic acid, methanol was used as solvent. The solvent choice is also influenced by cost, flash point, toxicity, solvency, and chain transfer efficiency.[2] Benzoyl peroxide was used as a free radical initiator. This compound is soluble in acrylic ester monomers and permits control of reaction and molecular weight of the product by selection and concentration of the initiator, monomer, and temperature employed during polymerization.[3]

EXPERIMENTAL

Materials

Methacrylic acid (MAA, Fluka grade), Methylmethacrylate (MMA, BDH grade), Benzoyl peroxide (Loba Chemie), and solvents (AR grade) were used.

Procedure

One-hundred mL of the purified monomers (composition given in Table I) was mixed with 400 mL methanol in a 3-necked, round bottom flask. The free radical initiator, benzoyl peroxide (1 g), was added to it. The flask was fitted with a reflux condensor and a mechanical stirrer, and was placed in a constant temperature bath at 80°C. The polymerization was monitored at regular intervals every 2 h by testing for the presence of free monomers by

thin layer chromatography (TLC). The mobile phase used was ether and hexane in 1 : 1 ratio, while the stationary phase was TLC-grade silica gel. An iodine chamber was used to develop the chromatoplate. The absence of a free monomer spot on the chromatoplate indicated the completion of the polymerization reaction.

The two copolymers that were synthesized by the above method are:

1. Polymer P_{30}, having 30% w/w of MAA in the monomer mixture.
2. Polymer P_{15}, having 15% w/w of MAA in the monomer mixture.

Isolation and Purification

The products, obtained from solution polymerization reaction, were isolated by precipitation using a nonsolvent, such as water. The precipitated product was filtered and washed several times with distilled water to remove traces of soluble impurities and residual methanol. The product was dried at 60°C. Further purification was carried out by redissolving the polymer in methanol and reprecipitating it in water. The optimum ratio of water to solution was 7 : 1. The filtered product was dried at 70°C overnight, was powdered, and was stored in air-tight containers.

Characterization of the Synthesised Polymers[4]

The physicochemical properties of polymers were elucidated and the results are recorded in Table II.

Table I Monomer Composition, Conditions, and Yields

Polymer	Monomer MMA	Quantity (g) MAA	Period of Heating (h)	% Yield
P_{30}	70	30	6	70.11
P_{15}	85	15	6	70.02

Table II Characterization of Copolymers

Polymer	Acid Number	Density[a] (g/mL)	R.I.[b]	Viscosity[c] Average (Mol wt $M \times 10^4$)	W_f (%)	T_g (°C)	Reduced Specific Viscosity (mL/g)
P_{30}	201.38	1.010	0.12	2.853	13.69	136.47	17.25
P_{15}	107.91	1.130	0.10	3.050	10.12	120.58	26.40

[a] Measured using standard specific gravity bottle.
[b] Recorded on Abbe's refractometer.
[c] Calculated from Mark–Houwink–Sakurada equation.[4]

Table III Composition of Film Casting Solution (25 mL)

Composition	Without PEG 4000	With PEG 4000	
P_{30}/P_{15} (g)	4.0	4.0	4.0
Triacetin (g)	1.6	1.6	1.6
PEG 4000 gm (% of Polymer Used)	—	0.05 (15%)	0.10 (25%)
Solvent[a] (mL to Make)	100	100	100

[a] Methanol in the case of P_{30} and acetone in the case of P_{15}.

Film Casting Evaluation

Films of varying thickness were casted on a mercury pool, as per the composition presented in Table III (petri dish area = 70.9 cm²).

Film Evaluation

Free films were evaluated for their solubility at different pH values, that is, at pH 2.2, 5.8, 6.8, and 7.4. The thickness
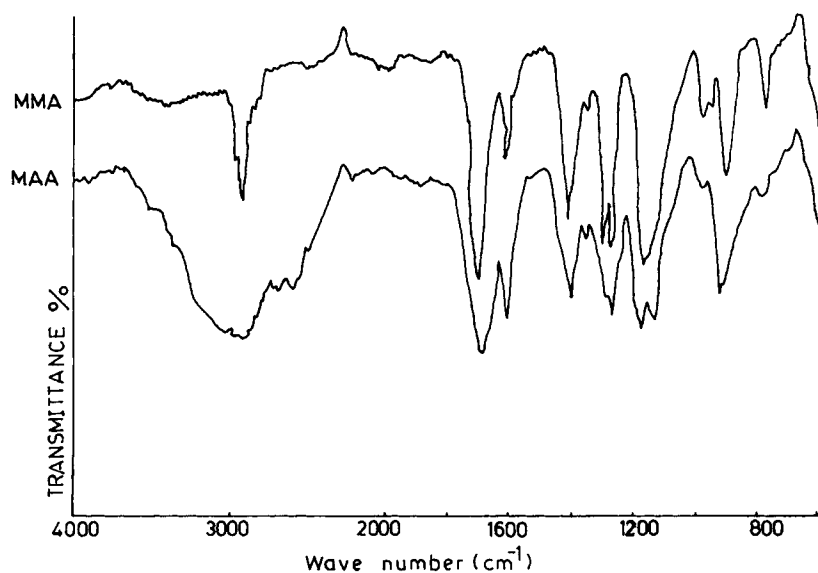
of films was measured on a micrometer screw gauge (Mitutoyo, Japan, least count = 0.01 mm). Mechanical properties such as stress, strain, and percent elongation at break of films (0.5 × 4 cm²), were evaluated on an Instron 1026 Tester.

Moisture Absorption

Accurately weighed films were exposed to relative humidity of 10%, 52%, and 75% for 1 month, in constant relative

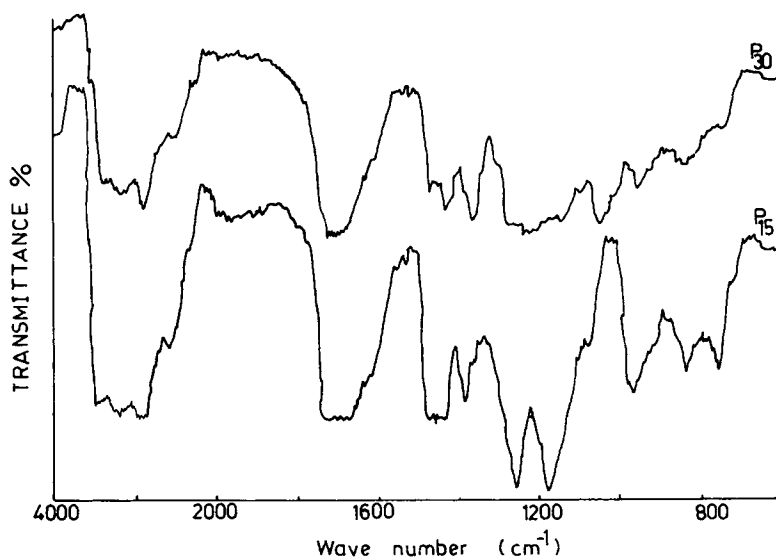**Figure 1** IR spectra of monomers.

Figure 2 IR spectra of polymers.

humidity chambers at room temperature. The % moisture absorption/desorption ($\%M_{AD}$) was calculated as follows.

$$\%M_{AD} = \frac{\text{wt of exposed film} - \text{Original wt of film}}{\text{Original wt of film}} \times 100$$

Water Vapor Transmission

The transmission cell was as designed by Patel and Leberger,[5] with suitable modifications.

A 30 mL screw cap bottle (circular aperture of diameter

Table IV Mechanical Properties of Free Films

Parameter	Copolymer	No PEG	PEG 12.5%	PEG 25%
Breaking	P_{30}	269.3 ± 0.41	139.15 ± 0.21	93.20 ± 0.07
Load "m" gm	P_{15}	269.3 ± 0.41	139.15 ± 0.21	93.20 ± 0.07
% Elongation at Break	P_{30}	132.9 ± 0.07	135.20 ± 0.06	152.80 ± 0.06
$\dfrac{\text{lb} - \text{lo}}{\text{lo}}$	P_{15}	138.0 ± 0.04	141.12 ± 0.04	145.00 ± 0.03
Stress "s"	P_{30}	4.256×10^{-7}	2.199×10^{-7}	1.473×10^{-7}
	P_{15}	2.620×10^{-7}	2.419×10^{-7}	1.935×10^{-7}
Strain "E"	P_{30}	1.329	1.352	1.520
	P_{15}	1.380	1.411	1.450

Table V Moisture Absorption/Desorption of Films of P_{30} (P_{15})

Time (days)	10% RH		52% RH		75% RH	
	Wt (g)	% MD	Wt (g)	% MD	Wt (g)	% MD
0	0.130 (0.378)	0 (0)	0.358 (0.184)	0 (0)	0.369 (0.353)	0 (0)
2	0.127 (0.374)	−2.00 (−1.01)	0.365 (0.185)	1.955 (0.54)	0.400 (0.357)	8.566 (1.13)
5	0.127 (0.374)	−2.00 (−1.01)	0.365 (0.186)	1.955 (1.08)	0.400 (0.363)	10.206 (2.83)
8	0.127 (0.374)	−2.00 (−1.01)	0.363 (0.186)	1.396 (1.08)	0.409 (0.369)	11.067 (4.53)
11	0.127 (0.374)	−2.00 (−1.01)	0.369 (0.187)	3.089 (1.63)	0.414 (0.373)	12.362 (5.66)
17	0.127 (0.374)	−2.00 (−1.01)	0.377 (0.190)	8.360 (3.26)	0.416 (0.373)	12.788 (5.66)
20	0.127 (0.374)	−2.00 (−1.01)	0.393 (0.192)	9.882 (4.35)	0.419 (0.373)	13.585 (5.66)
26	0.127 (0.274)	−2.00 (−1.01)	0.393 (0.192)	9.882 (4.35)	0.424 (0.373)	15.002 (5.66)

Table VI Water Vapor Transmission of Free Films

Copolymer Thickness (mm) Time (h)	P_{30}						P_{15}	
	0.027	0.044	0.135	0.155	0.052	0.076	0.106	0.135
	Weight of Transmission Cell[a] (g)							
0	52.48	55.33	52.46	55.34	55.44	55.99	52.35	52.64
24	52.41	55.29	52.44	55.32	55.41	55.96	52.34	52.63
48	52.36	55.23	52.42	55.31	55.37	55.93	52.31	52.61
72	52.31	55.19	52.40	55.29	55.33	55.90	52.30	52.60
96	52.25	55.14	52.38	55.28	55.30	55.87	52.28	52.59
120	52.21	55.10	52.36	55.26	55.26	—	52.25	52.58
W (g/h)	-2×10^{-3}	-2×10^{-3}	-9.0×10^{-4}	-6.4×10^{-4}	-1.5×10^{-3}	-1.2×10^{-3}	-8.8×10^{-4}	-4.9×10^{-4}
R[b]	4.2×10^{-5}	4.1×10^{-5}	1.9×10^{-5}	1.3×10^{-5}	3.2×10^{-5}	2.5×10^{-5}	1.8×10^{-5}	1.0×10^{-5}
R[c]	0.1005	0.0981	0.0452	0.0321	0.0775	0.0592	0.0441	0.0245

[a] $W = \dfrac{y_2 - y_1}{x_2 - x_1}$, where y = Wt of transmission cell (g); x = time (h).

[b] $R = W/A\Delta P$, where A = area of exposed film = 1.65 cm², ΔP = vapor pressure gradient across film = 28.96 mm of Hg.

[c] $R' = 2000\ R = R$ for 24 h for 100 cm² film (g/24 h for 100 cm² × mm of Hg).

1.5 cm) was filled with 5 mL of supersaturated solution of sodium-d-tartarate (yielding a % RH of 91% at 30°C and exerting a vapor pressure of 28.96 mm² of Hg[6]). The film was placed between two gaskets (aperture diameter 1.45 cm) and was tightly sealed on the bottle with adhesive tape. The assembly was placed in a dessicator over calcium chloride at room temperature and was allowed to equilibrate for 24 h. The decrease in weight, after every 24 h, was recorded on an Owalabar single pan balance.

$$R = W/A\Delta P$$

where R is the amount of moisture transmitted per unit time through a film of unit area, when exposed to a vapor pressure gradient of 1 unit and expressed in g/h × cm² × mm of Hg at 30°C, W is the amount of moisture transmitted per unit time (g/h), obtained from the slope of a plot of transmission cell (g) vs. time (h), A is the area of the exposed film (cm²), and ΔP is the vapor pressure gradient across film (mm of Hg).

RESULTS AND DISCUSSION

Since azobisisobutyronitrile (AIBN), a widely used free radical initiator, produced low yields, benzoyl peroxide was used to produce good yields of copolymers. The acid number of P_{30} was higher than P_{15}, because of the higher concentration of MAA in the former. The percent water fraction, upon hydration, indicates the hydrophilicity of the polymer. An increase in the acid content brings about an increase in W_f, hence the higher value of $\% W_f$ for P_{30}. All three types of polymers show (Figs. 1 and 2) C — H stretching, —COOR, —CH₃, —CH₂, and the skeletal — C — C — C — chain functions. IR of MMA and MAA, in addition, show a band at 1430 and 1420 cm⁻¹ that is characteristic of a geminal disubstituted alkene. The absence of these bands in the spectra of the synthesized polymers indicates that polymerization has occurred via opening of the double bonds, thus giving the structure:
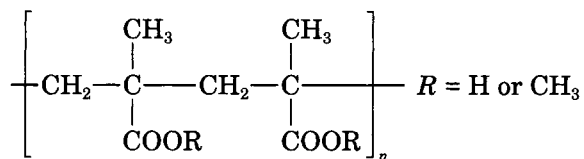
Films of both copolymers were insoluble in buffer solutions of pH 2.2 and 5.8, however, at pH 6.8 and 7.4, the solubility was considerably higher. The mechanophysical properties are shown in Table IV.

As evident from Table IV, the addition of PEG increases the breaking load and stress and decreases the relative values of percent elongation at break and strain. All the films showed excellent flexibility, since no detectable signs of damage in the form of cracks, splits, or breaking of the films were observed during the folding endurance test.

According to Table V, moisture desorption was observed at 10% RH, whereas films at 52% and 75% RH showed moisture absorption. On a comparative basis, films of P_{30} showed greater moisture absorption, due to its greater hydrophilicity, thus attracting more water molecules. Table VI shows that the R value decreases as the film thickness increases. Also, R values for P_{30} were more than for P_{15}, because of their hydrophilic characteristics, which cause water molecules to penetrate more rapidly through the film than those containing lipophilic groups.

CONCLUSIONS

The synthesized polymers showed good mechanical and physical properties. These polymers, therefore, can be used to give a controlled release profile, where pH dependency is required. Their application can be extended to various fields of agrochemicals and pharmaceuticals, where a sustained release mechanism is required.

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